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Chemical and Electronic Structure Analysis of a SrTiO₃ (001) / *p*-Ge (001) Hydrogen Evolution Photocathode

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Abstract (100 words)

Germanium is a small-gap semiconductor that efficiently absorbs visible light, resulting in photoexcited electrons that are predicted to be sufficiently energetic to reduce H₂O and evolve H₂ gas. In order to protect the surface from corrosion and prevent surface charge recombination in contact with aqueous pH 7 electrolyte, we grew epitaxial SrTiO₃ layers of different thicknesses on *p*-Ge (001) surfaces. 4 nm SrTiO₃ allows photogenerated electrons to reach the surface and evolve H₂ gas, while 13 nm SrTiO₃ blocks these electrons. Ambient pressure X-ray photoelectron spectroscopy indicates the surface readily dissociates H₂O to form OH species, which may impact surface band bending.

Keywords electrochemical synthesis; surface chemistry; Ge

Introduction

The direct conversion of solar energy to chemical fuels is a tantalizing route to store renewable energy. By employing photocatalysts to split water into H₂ and O₂ gas,^[1-2] this can be achieved in a cycle free of CO₂ emissions. A ‘Z-scheme’^[3-4] separates the two constituent reactions—the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER)—so that

they occur on separate electrodes, thus decoupling the requirements of band gap and the energy of photoexcited carriers in materials design. Typical oxide photoanodes used to drive the OER have large band gaps,^[5-7] and can thus absorb high-energy photons in a photoelectrochemical (PEC) device, allowing low-energy photons to pass through to the photocathode, which drives the HER.

One semiconductor with attractive light-absorption properties is Ge. In contrast to other semiconductors currently being studied, Ge has a small, indirect band gap of 0.66 eV, as well as a larger optical absorption coefficient across the visible portion of the solar spectrum and into the infrared.^[8] Furthermore, Ge exhibits high room-temperature electron and hole mobilities of 3900 and 1900 cm²/V-s, respectively.^[9] Density functional theory (DFT) calculations indicate that the conduction band of Ge is higher in energy than hydrogen redox,^[10] indicating photoexcited electrons are energetic enough to reduce H₂O to evolve H₂ gas. However, interaction with the electrolyte can lead to corrosion of the Ge surface^[11] and recombination of photogenerated electron-hole pairs at surface states,^[12] limiting PEC activity.

We employ controlled passivation^[13] of Ge by epitaxial growth of a wide band-gap semiconductor, SrTiO₃, using oxide molecular beam epitaxy (MBE). By examining a model epitaxial film, we are able to examine charge transport through the heterostructure to yield a critical new understanding of PEC. A similar approach has recently been employed to protect a GaAs photovoltaic.^[14] Growth of SrTiO₃ on Ge has previously been demonstrated for the purpose of investigating associated electrical properties,^[15-16] and we have recently measured the valence band (VB) offset between Ge and SrTiO₃.^[17] These findings support the idea that photoexcited electrons in the Ge would have a downhill path in energy to reach the SrTiO₃ surface.

Here we present the first PEC measurements of the HER on a SrTiO₃ (001) / *p*-Ge (001) heterostructure in neutral (pH 7) electrolyte. This model epitaxial system enables quantification of the abrupt interface by scanning transmission electron microscopy (STEM), as well as surface stoichiometry and speciation both post mortem, following electrochemical cycling, and *in situ* using ambient pressure X-ray photoelectron spectroscopy^[18] (AP-XPS). The Sr/Ti ratio remains similar under all conditions, suggesting the SrTiO₃ film is stable in the electrochemical environment and supporting its role as a protective cap on Ge, and that the surface actively dissociates H₂O to form OH groups. Surface roughness on the Ge substrate leads to pinhole defects which hinder the efficacy of 4-nm SrTiO₃ film passivation; however, a 13 nm SrTiO₃ film blocks electron transport to the surface. These findings suggest that tailoring SrTiO₃ electronic properties by, for example, doping, may provide a promising route for Ge photocathode protection.

Experimental Details

Film Growth

Ga-doped *p*-Ge (001) substrates (AXT Inc., $\rho = 0.04 \text{ } \Omega\text{-cm}$) were prepared by wet etching procedures described elsewhere.^[19] Following desorption of the chemically prepared oxide at ~600 °C, the surfaces were clean at the detection limit of X-ray photoelectron spectroscopy (XPS) and exhibited a (2×1) reconstructed surface. Epitaxial growth by oxygen assisted MBE followed the approach outlined in Jahangir-Moghadam et al.^[20], as further detailed in Ref. ^[17]. An initial SrGe₂ (001) (3×1) layer was grown at 400 °C in vacuum, followed by the growth of 3 unit cells (u.c.)

amorphous SrTiO₃ at ambient temperature in 4×10^{-7} Torr O₂, followed by subsequent crystallization at 600 °C in vacuum. Additional layers were grown at 300 °C in O₂ and annealed at up to 500 °C in vacuum to achieve better crystallinity, reaching a final thickness of 5 u.c. (2 nm), 4 nm, or 13 nm SrTiO₃.

Scanning Transmission Electron Microscopy

Cross-sectional scanning transmission electron microscopy (STEM) samples were prepared using an FEI Helios NanoLab Dual-Beam Focused Ion Beam (FIB) microscope and a standard lift out procedure along the Ge [100] and [110] zone axes, with initial cuts made at 30 kV / 2° and final polishing at 1 kV / 3° incidence angles. High-angle annular dark field (STEM-HAADF) images were collected on a JEOL ARM-200CF microscope operating at 200 kV, with a convergence semiangle of 20.6 mrad and a collection inner semiangle ranging from 68–90 mrad. To minimize scan artifacts and improve signal-to-noise, drift-corrected images were prepared using the SmartAlign plugin;^[21] for this, a series of 10 frames at 1024 x 1024 pixels with a fast 2 μs px⁻¹ dwell time and 90° rotation between frames was used. The frames were upsampled 3x prior to non-rigid alignment. The inset of Figure 1c was subsequently processed using a lattice enhanced filter to improve signal-to-noise.^[22]

Electron energy loss spectroscopy (STEM-EELS) maps were collected on a Nion UltraSTEM 100MC “Hermes” microscope operating at 60 kV with a convergence semiangle of 31 mrad and a 44 mrad STEM-EELS collection angle. STEM-EELS maps were collected using 0.37 eV ch⁻¹ dispersion, yielding an effective energy resolution of ~1.1 eV. No plural scattering correction was performed, since zero loss measurements confirm that the samples are sufficiently thin ($t/\lambda < 0.5$ inelastic mean free paths). Unprocessed composition maps are presented in the supplementary information.

Photoelectrochemistry

Films were transferred directly from UHV to a N₂-purged glove box for PEC measurements. GaIn eutectic (Sigma, >99.99%) was scratched into the back of the Ge, and a Cu wire held in contact with the pad in a custom build compression cell. The electrolyte was prepared from Nanopure water (18.2 MΩ-cm) from a mixture of K₂HPO₄ and KH₂PO₄ (Sigma, >99.0%) to achieve a pH of 7 and phosphate concentration of 0.1 M, and bubbled with ultra-high purity N₂ gas before and during data collection. Measurements were made with a CHI-660C potentiostat by cyclic voltammetry at 20 mV/s or constant potential measurements, and voltages corrected for the electrolyte resistance between the working and reference electrodes (~95 Ω for 4 nm SrTiO₃/Ge). The saturated calomel reference electrode (RE-2BP, ALS Co.) was calibrated to the reversible hydrogen electrode (RHE) scale in the same electrolyte, saturated with H₂ and using Pt working and counter electrodes. A Pt counter electrode (ALS Co.) was also used for PEC measurements.

Light from a 630 nm ultra-high power LED (Prizmatix) was incident through a planar quartz window. The illuminated area of the sample was defined by the PEEK holder, and was commensurate with the area exposed to the electrolyte. The intensity of the LED at the location of

the sample was measured after passing through the quartz window with a Newport 843-R power meter, and estimated to attenuate ~10% over the ~6 cm path length from water absorption.

X-ray Photoelectron Spectroscopy

Characterization of the films as-grown and after (photo)electrochemical cycling was performed with an Al K-alpha source in UHV at room-temperature.

Ambient pressure X-ray photoelectron Spectroscopy (AP-XPS) was collected at Beamline 9.3.2 at Lawrence Berkeley National Laboratory's (LBNL) Advanced Light Source (ALS).^[23] 5 u.c. SrTiO₃/Ge was placed directly onto a ceramic heater, held in place by spring-loaded Inconel tips separated with an Al₂O₃ spacer, and grounded through the thermocouple. The thermocouple was pressed into a gold foil placed directly onto the sample surface and isolated from the sample holder clip with an Al₂O₃ spacer.

The incident photon energy was calibrated to the Au 4f_{5/2} peak at 84 eV binding energy (BE). The sample was first heated to 300 °C in 100 mTorr O₂ (measured by a calibrated membrane pressure gauge) and characterized. Keeping the sample at 300 °C, the chamber was evacuated to a pressure lower than 1.5×10^{-7} Torr, and 100 mTorr H₂O was introduced into the chamber. The water source was prepared from deionized water (Millipore, >18.2 MΩ·cm) and degassed by several freeze-pump-thaw cycles. The sample was then cooled in 100 mTorr H₂O.

O 1s spectra were deconvoluted with Gaussian-Lorentzian (GL) peaks using CasaXPS after a Shirley-type background subtraction (**Table S1**). The O 1s integrated area of the (bi)carbonate peak was calculated from the area of the C 1s (bi)carbonate peak using an O 1s:C 1s relative sensitivity factor, which was experimentally calibrated using the core levels of CO₂ gas.^[24]

Results

Figure 1 shows representative cross-sectional STEM-HAADF images that illustrate the quality of the SrTiO₃ (001) / *p*-Ge (001) film and interface. We observe a relatively uniform film across large areas, as shown in the image of a 13 nm SrTiO₃ / Ge interface in Figure 1a. We observe no phase separation or impurities, but we do measure some substrate roughness in Figure 1b. This roughness is accompanied by film discontinuities and the presence of antiphase boundaries (see inset of Figure 1c). We note that the damage at the film surface (top) in this image is the result of long exposure to the electron beam and not characteristic of the film itself.

We found that this structure is extremely beam sensitive and that exposure to the electron beam over 30–60 seconds was sufficient to locally amorphize the structure. To mitigate this problem, we conducted multi-frame, drift-corrected imaging using the SmartAlign plugin^[21, 25] to reduce the effective electron dose rate; this approach allowed us to acquire high-resolution images of the film-substrate interface without damaging the underlying structure. Figure 1c shows that the interface is extremely abrupt, a finding further supported by STEM-EELS maps of a related 5 u.c. SrTiO₃ / Ge heterostructure shown in Figure S1. Taken together, our results illustrate the uniformity, relatively good quality, and sharp interface structure that can be attained through MBE growth of these films.

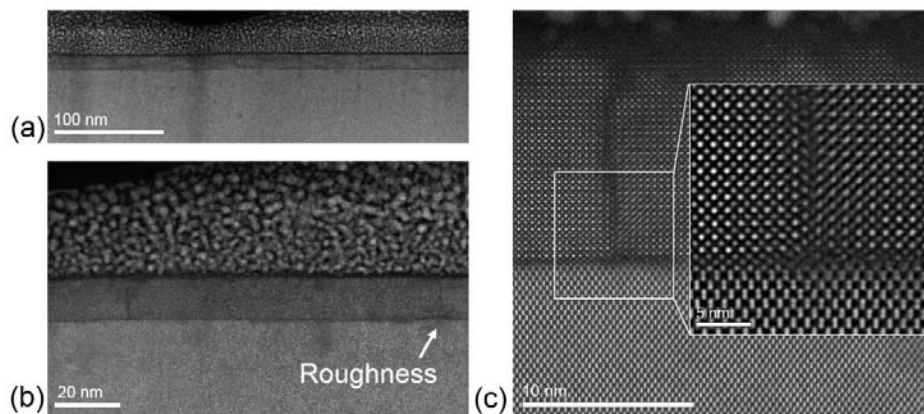


FIG. 1. (a) Representative cross-sectional STEM-HAADF image of a 13 nm SrTiO₃ / *p*-Ge (001) heterostructure, showing the overall structure. (b) STEM-HAADF image of local Ge substrate roughness. (c) Drift-corrected STEM-HAADF image of a film discontinuity and lattice-filtered inset of an antiphase boundary between two film regions.

The band alignment at the SrTiO₃ / Ge interface is of critical importance for separation of photogenerated electrons and holes, and the transport of electrons to the surface to reduce H₂O and generate H₂. Previous measurement of the core levels and valence band (VB) by XPS^[17] indicate the VB of SrTiO₃ is 3.0 eV lower in energy than that of *p*-Ge. Coupled with the 3.25 eV band gap of SrTiO₃ and the 0.66 eV band gap of Ge, the conduction band (CB) of SrTiO₃ is found to be 0.4 eV below that of Ge. DFT band edge calculations report the Ge CB to be -0.9 V vs. NHE at pH 0,^[10] placing the CB of SrTiO₃ in the heterostructure at -0.5 V vs. NHE (Figure 2). This is in contrast to the CB of isolated SrTiO₃, reported at -0.26 V vs. NHE at pH 0.^[4] Assuming a Nernstian shift of the oxide band edges with pH,^[26] this finding then suggests the CB of the SrTiO₃/Ge heterostructures is at -0.5 V vs. RHE in pH 7, resulting in photoexcited electrons being sufficiently energetic to drive the HER.

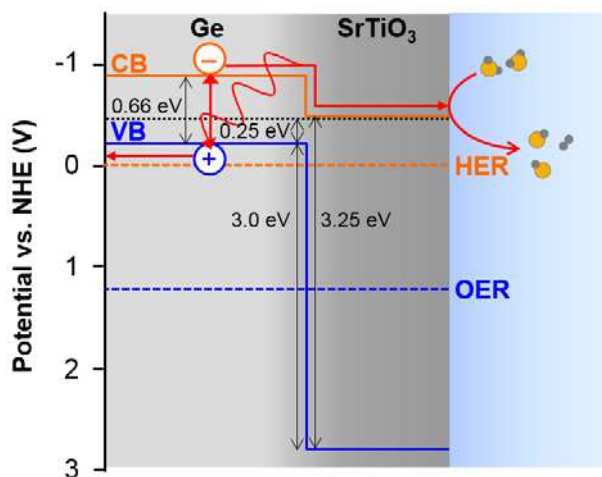


FIG. 2. Interface band energy alignment on the NHE scale (pH = 0), obtained from the experimental measurement of VB offset in the heterostructure,^[17] reported CB level of Ge^[10] and

band gap of SrTiO₃. For pH 7 conditions, assuming Nernstian behavior of the oxide band edges would then result in a SrTiO₃ CB at -0.5 V vs. RHE.

Following growth, the heterojunctions were transferred directly from UHV to a N₂-purged glove box for electrochemical characterization in a custom 3-electrode cell. The pH 7 phosphate-buffered electrolyte was constantly bubbled with N₂ before and during measurements to minimize buildup of evolved H₂ gas. Figure 3 a compares the cyclic voltammetry for 4 nm and 13 nm SrTiO₃ on Ge, measured initially in the dark. For the 4 nm film, cathodic current was observed commensurate with the formation of bubbles on the electrode with an onset potential \sim -0.7 V vs. RHE in the dark. For the 13 nm film, current was negligible within the tested window. We hypothesize the 13 nm film acts as a blocking electrode for photogenerated electrons as seen by the larger resistance measured by high frequency impedance spectroscopy at open circuit conditions ($> 400 \Omega$, compared to $< 100 \Omega$ for the 4 nm heterostructure).

Films were then removed from the electrolyte within the purged N₂ box, rinsed with DI water, dried, and returned to UHV for XPS characterization. XPS confirms no electrodeposition of Pt or other contaminants on the film (Figure S2-S3). The ratio of Sr 3d to Ti 2p core levels remained similar to that of the as-prepared film (Figure 3b), indicating no preferential leaching of e.g. Sr occurred. This is in contrast to thermodynamic calculations of the Pourbaix diagram at pH 7 which indicate a greater stability of TiO₂ with Sr cations compared to SrTiO₃,^[27] and suggests additional contributors to kinetic stabilization like surface energy and functionalization play an important role. We note, however that the ratio of the Sr 3d and Ti 2p relative to the Ge 3d for the 4 nm film (where the Ge 3d is observable due to the large probe depth of the > 1400 eV kinetic energy photoelectrons) decreased after cycling (Figure S4), suggesting the roughness of the Ge substrate may expose some pinholes defects in the SrTiO₃ film which grow with cycling.

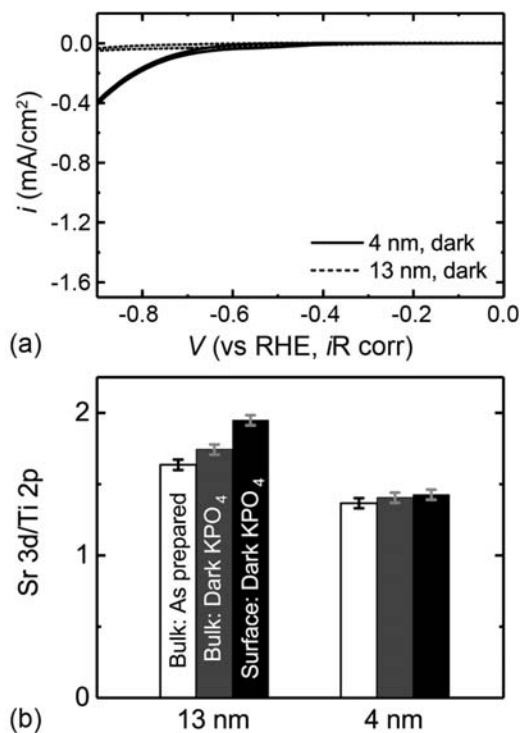


FIG. 3. (a) CV curves in dark at 20 mV/s in pH 7, 0.1 M phosphate buffer. The 13 nm SrTiO₃ (solid) acts as a blocking electrode, while the 4 nm film (dashed) allows current to be passed to drive HER at high overpotentials. (b) XPS ratio of Sr 3d/Ti 2p core levels measured with $h\nu = 1486$ eV for the as prepared heterostructure (white) and after cycling in the dark. At 90° incidence (“bulk”) the probe depth is ~ 7 nm, while at 20° incidence (“surface”) it is ~ 2 nm.

Upon illumination with an ~ 8 mW 630 nm LED (Figure 4a), the 13 nm SrTiO₃/Ge heterostructure exhibited no change in current density compared to cycling in the dark. In contrast, the 4 nm SrTiO₃/Ge heterostructure exhibited a cathodic photocurrent after initially sweeping below ~ -0.75 V vs. RHE. The photocurrent increased with cycle number; however, the dark current remained constant before and after cycling. We hypothesize this behavior might result from *in situ* generation of oxygen vacancies in the SrTiO₃ film, which would facilitate electron transport to the surface. Chronoamperometry (Figure 4b) illustrates the photocurrent from the 4 nm SrTiO₃/Ge heterostructure directly by turning switching the LED on and off, in contrast to the lack of HER photocurrent from a bare Ge wafer (Figure S5). The difference between the dark current just before 200 s and the current during illumination after 200 s (where the noise arises from the rapid generation of H₂ bubbles and light scattering) gives a photocurrent of 1.1 mA/cm² at -0.87 V vs. RHE. This corresponds to an incident-photon-to-current efficiency (IPCE) of ~ 14 %. We note that the epitaxial nature of the film on the single crystal Ge substrate results in a roughness factor approaching unity and a highly reflective surface; thus the photocurrent on a geometric basis and IPCE would be expected to improve greatly by introducing nanostructuring.^[28] Furthermore, the high overpotential is expected to decrease substantially upon incorporation of a cocatalyst.^[29-31]

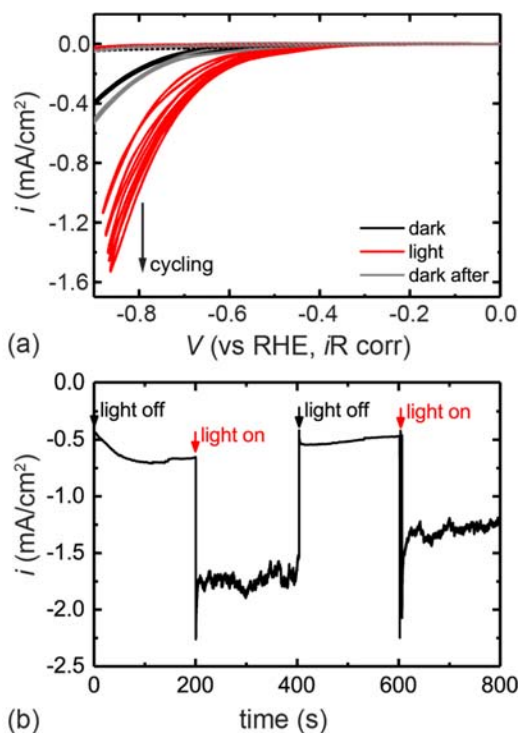


FIG. 4. (a) CVs at 20 mV/s in pH 7, 0.1 M phosphate buffer for the 13 nm SrTiO₃ (dashed) and 4 nm SrTiO₃ (solid) on Ge. Compared to polarization in the dark (black), illumination with a 630 nm LED (red) causes a photocurrent/voltage for the 4 nm film, which increases with cycling. After illumination (gray), the CV is similar to before illumination. (b) Chronoamperometry for 4 nm SrTiO₃ / Ge at -0.87 V vs RHE. The dark HER current initially increases, and illumination leads to a constant -1.75 mA/cm² current. Turning the light off returns the current to that previously measured in dark. Repeated illumination gives a similar photocurrent, however this decreases over time.

The activity of the 4 nm SrTiO₃ / Ge heterostructure decreased with time. Following removal from the cell and copious rinsing to remove salt before introduction to the UHV chamber for XPS, much of the film delaminated, suggesting that pinhole defects in the 4 nm film arising from roughness of the Ge crystal grow with cycling. In contrast, the 13 nm SrTiO₃ film shows comparable ratios of Sr 3d and Ti 2p and remains sufficiently thick that no Ge 3d is observed following cycling under illumination (Figure S6). Future directions will include cation-doping of thicker SrTiO₃ films to ensure *n*-type conductivity persists over the conformal film thickness.

In order to better understand the interface between SrTiO₃ and the electrolyte, we performed ambient pressure X-ray photoelectron spectroscopy (AP-XPS) in both dry-oxidizing and humid-reducing environments. The tunable incident photon energy (IPE) at a synchrotron allows the probe depth to be tuned to the top ~1 nm of the film ($h\nu = 690$ eV, O 1s core level), and a system of differential pumping and electrostatic lensing enables the surface speciation to be probed in equilibrium with a gas.^[18]

We first consider the surface at 300 °C in 100 mTorr of O₂, similar to growth conditions, which minimizes carbon present from transferring the samples between growth facilities and the synchrotron (Figure S7). Figure 5 illustrates that the O 1s spectra is dominated by bulk-coordinated oxygen of the perovskite crystal,^[24] with some residual CO₃ whose intensity is scaled from that of the CO₃ feature in the C 1s inset. When the O₂ is removed from the chamber and H₂O slowly introduced, a feature increases in intensity at ~1.2 eV binding energy (BE) above the bulk (Figure S8). This feature is attributed to hydroxyl, OH, formation from the dissociation of H₂O on the surface.^[24] In a humid environment, a feature (“Surf”) at higher BE above the bulk is notable, observed from depth profiling (Figure S9) to be located at the surface. A feature at similar BE offsets located on the surface has been observed for (001)-oriented LaFeO₃ films terminated with the “LaO” plane, but not for the “FeO₂” plane,^[32] We note, however, that on the SrTiO₃ surface, a small phosphorous signal (likely in the form of phosphate) was observed in humid environments (Figure S7), and may also contribute to the signal at this intensity. Adsorption of phosphate species in humid environments may also have implications on the use and role of a PO₄-containing buffer during PEC measurements.^[33]

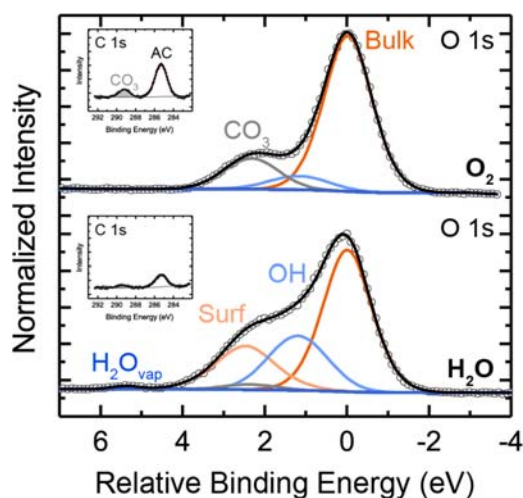


FIG. 5. AP-XPS performed at an incident photon energy (IPE) of $h\nu = 690$ eV at 300 °C in 100 mTorr O₂ (top) or 100 mTorr H₂O (bottom). The O 1s spectra is shown on a binding energy (BE) scale relative to bulk oxygen (orange), with OH (light blue), CO₃ (gray, intensity determined from the shaded CO₃ feature in the C 1s inset), surface oxygen (peach), and H₂O_{vapor} (medium blue) at increasingly higher BE. Some adventitious carbon (AC, C 1s inset) remains and attenuates the spectra. Fitting parameters are given in Table S1.

The notable dissociation of H₂O on the surface of SrTiO₃ to form OH species suggests that during PEC conditions in a neutral electrolyte, SrTiO₃ is likely also hydroxylated. This adsorption of OH species may in turn impact band bending at the surface, of future interest for studies linking surface speciation to the driving force for charge transfer during PEC. In further consideration of the surface stoichiometry in equilibrium with gaseous environments, the ratio of Sr signal to combined Sr and Ti signals remains relatively constant across both dry-oxidizing and humid-reducing conditions, as does the distribution of Sr and Ti with depth (Figure S10). This further supports *ex situ* measurements after electrochemically cycling, which indicate Sr remains stable within the SrTiO₃ film in contact with H₂O at pH 7.

Conclusions

SrTiO₃ was epitaxially grown on *p*-Ge (001) using MBE as a means to protect the surface of the Ge photoabsorber during PEC measurements in aqueous pH 7 electrolyte and maintain an energetically downhill path for photogenerated electrons to reach the solution. The band alignment between SrTiO₃ and Ge is such that photoexcited electrons can travel through a 4 nm SrTiO₃ capping layer and remain sufficiently energetic to reduce H₂O and evolve H₂ gas in the HER reaction. For 13 nm SrTiO₃, the film behaves like a blocking electrode, with larger contact resistance and minimal current passed at similar overpotentials compared to the 4 nm film. At -0.87 V vs RHE, the IPCE for 630 nm red light is ~14%, noting that the roughness factor of the epitaxial film approaches one and notable reflective losses are not considered in calculation of the IPCE. Thus, the current density would be expected to improve with nanostructuring. Furthermore, the electrode is free of Pt or any other catalyst, and thus its probed intrinsic ability to supply photoexcited electrons to the HER is expected to notably improve upon deposition of a co-catalyst.

Some inherent roughness (on the nm scale) on the Ge surface leads to the presence of pinhole defects in the 4 nm film, resulting in corrosion and film delamination. Future directions include La doping of the SrTiO₃ films to control their carrier concentration such that thicker conformal films can be epitaxially grown and maintain sufficient conductivity for charge transfer.

In situ characterization of the SrTiO₃ (001) / *p*-Ge (001) heterostructure provides insight into the surface speciation during reaction conditions. AP-XPS was used to characterize the surface under dry-oxidizing and humid-reducing conditions. In contrast to the dry O₂ environment, in a humid environment SrTiO₃ notably dissociates H₂O to form OH species. This indicates that during the HER in pH 7 aqueous electrolyte, the SrTiO₃ surface likely also contains some hydroxyl species. Future directions will link this speciation to the resultant surface band bending.

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